Insights into the mechanism for gold catalysis: behaviour of gold(i) amide complexes in solution

Article (Published Version)

Dalton Transactions

RSC Publishing

PAPER

View Article Online
View Journal

Insights into the mechanism for gold catalysis: behaviour of gold(I) amide complexes in solution†

Cite this: DOI: 10.1039/c3dt33039g

Mariusz Bobin, Iain J. Day, Stephen M. Roe and Eddy M. E. Viseux*

Received 19th December 2012,
Accepted 25th February 2013

DOI: 10.1039/c3dt33039g

www.rsc.org/dalton

We report the synthesis and activity of new mononuclear and dinuclear gold amide complexes **1–7**. The dinuclear complexes **6b** and **7** were characterised by single crystal X-ray analysis. We also report solution NMR and freezing point depression experiments to rationalise their behaviour in solution and question the de-ligation process invoked in gold catalysis.

Introduction

The applications of gold(I) catalysis in methodology and synthesis have seen a remarkable growth in recent years[1] following Schwemberg's perchlorination of naphthalene in 1935.[2] Most mechanisms have involved a cationic gold species usually from chlorine abstraction by a silver salt,[3] protonolysis of an alkyl gold[4] or ligand dissociation in solution prior to alkene complexation. The cationic nature was further demonstrated by Widenhoefer who reported the results of X-ray diffraction experiments on cationic gold(I) complexes derived from a series of alkynes.[5] The loss of an X-ligand to generate an active gold intermediate combined with a limited coordination sphere due to relativistic considerations and radial contraction on gold(I) complexes have also driven the development of chiral gold(I) complexes LAuX with structural modification of the L-ligand and rare examples of chiral X-ligands; in the latter case, the efficiency heavily relies on the nature of the solvent.[1,6]

Many tri- and tetra-coordinate gold complexes have been reported.[2–4,7–21] Most notably, Hashmi reported the X-ray crystallographic characterisation of a tri-coordinate gold(I) complex L_2AuX,[5,9] and many polynuclear auracyclic complexes featuring bidentate ligands have been described extensively and such systems often include Au–Au interactions.[8] For all the evidence for complexes which, in the solid state, display coordination numbers for gold that exceed two, the rationalisation of gold catalysis in solution rarely invokes species with coordination numbers that exceed two unless they are hypothesised in transition states of complex-induced activation reactions.[5,7,8,22–24] Despite the ever-growing database of transformations catalysed by gold(I) and the proposed cationic nature of the complex in these transformations, little experimental information is available regarding the existence in solution of a tricoordinate gold species and the general nature of gold complexes in solution.

We describe herein our routes to catalytically active gold amide complexes LAuX featuring either modified L or X ligands, as well as binuclear complexes. These results can potentially be used to access structurally diverse gold amide or peptide complexes. This opens up possibilities for structural modifications and drug design of organogold complexes, as the routes are amenable to combinatorial chemistry and parallel synthesis. We also examined the de-ligation process of such amide complexes in the initial mechanistic step of gold catalysed transformations. To this end, we report on the investigation of the behaviour of these complexes in solution with NMR and freezing point depression studies and contrast the results with the standard mechanistic proposal involving a cationic gold intermediate.

Results and discussion

In our search for rapid routes to libraries of gold complexes, we investigated the influence of the gold amide bond on the catalytic activity of complexes that contain this moiety for cycloisomerisation reactions in solution. Initial models included chiral gold amides as described in Fig. 1.

Catalytic activities

The investigation of the connectivity of the gold–ligand complex is a necessary step prior to the mechanistic investigation, and notably rationalising the influence of the electronegative nature of the *N*-derived X-ligands on both the reactivity and the stability of gold amide complexes is crucial. The initial design of **8**, featuring a gold *N*-alkyl triflic amide linkage, showed no catalytic activity (Fig. 1) when evaluated in two model reactions, a

School of Life Sciences, Department of Chemistry, University of Sussex, Brighton, BN1 9QJ, UK. E-mail: e.m.e.viseux@sussex.ac.uk; Tel: +44 (0) 1273 678621

†Electronic supplementary information (ESI) available: NMR spectra for all compounds and X-ray crystallographic studies for compounds **6b** and **7** are included. CCDC 915634 and 916508. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33039g

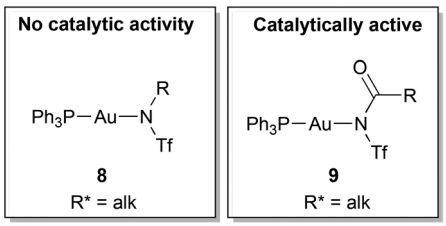
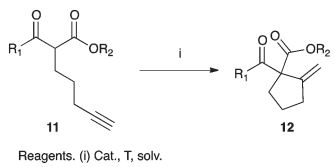


Fig. 1 General model for gold amide complexes ($T_f = CF_3SO_2$).



Scheme 1 Cyclopentannulation of β-ketoester **11**.

Table 1 Gold catalysed Conia-ene cyclopentannulation

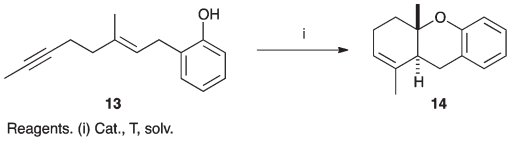
	Cat.	Mol%	Solv.	Time [h]	T [C°]	Yield [%]
1	**2**	2[c]	DCM	48	RT	73[b]
2	**2**	2	DCM	48	RT	65[b]
3	**2**	1	DCE	24	50	58[b]
4	**7**	5	DCM	120	RT	33[b]
5	**7**	5	DCE	14	70	75[b]
6	**7**	5	DCE	120	70	91[a]
7	**5a**/**5b**	2.5	DCM	168	RT	/[a]
8	**5a**/**5b**	2.5	DCE	168	70	52[a]
9	**6a**/**6b**	5	DCM	168	RT	/[a]
10	**6a**/**6b**	5	DCE	168	70	51[a]
11	/	/	DCE	24	50	8[b]
12	/	/	DCE	14	70	13[b]
13	/	/	DCE	48	80	/[a]
14	**15**	5	DCM	72	RT	/[b]
15	**15**	5	DCE	96	50	/[b]
17	**10**[d]	5	DCM	120	RT	/[b]
18	**10**[d]	5	DCE	120	70	/[b]
19	**10**[e]	5	DCM	120	RT	/[b]
20	**10** + **15**	5 + 20	DCM	120	RT	/[b]
21	**10** + **15**	5 + 5	DCE	120	50	/[b]
22	**3**	5	DCM	120	RT	96[b]
23	**4**	5	DCM	98	RT	90[b]

[a] **12b**: R^1 = Ph, R^2 = Et. [b] **12a**: R^1, R^2 = Me. [c] 1 mol% was initially added, followed by an extra 1 mol% after 24 h. [d] L-Proline was added (0.2 equiv.). [e] L-Proline was added (1 equiv.).

modified Conia-ene cyclopentannulation (Scheme 1, Table 1)[25] and a phenol enyne cycloisomerisation (Scheme 2, Table 2).[26] The influence of electron-withdrawing substituents on the nitrogen was found to have a critical impact on the outcome of these reactions (Fig. 1). Switching to an *N*-triflic alkanamide **9** dramatically improved the reactivity and the yields were comparable to those obtained with bis-triflic amide complex $Ph_3PAuNTf_2$ **10** reported by Gagosz[3] (Scheme 1, Table 1) (Fig. 2).

Cyclic gold complex *vs.* linear gold complexes *vs.* naked ligand

The standard mechanistic proposal for catalytic and stoichiometric reactions of this type begins with dissociation of the



Scheme 2 Cycloisomerisation of enyne **13**.

Table 2 Gold catalysed cycloisomerisation of an enyne

	Cat.	Mol%	Solv.	Time [h]	T [C°]	Yield [%]
1	**7**	5	DCM	168	RT	55
2	**2**	2	DCM	48	RT	67
3	**5a**/**5b**	2.5	DCM	168	RT	/
4	**3**	5	Benzene	120	RT	63
5	**3**	5	DCM	120	RT	78
6	**4**	5	DCM	120	RT	46

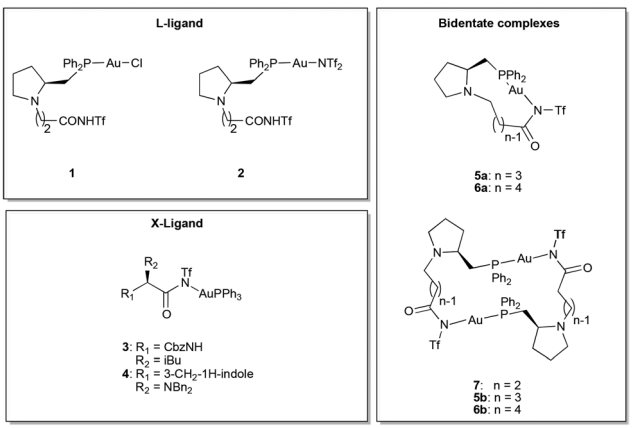


Fig. 2 Summary of the gold amide complexes.

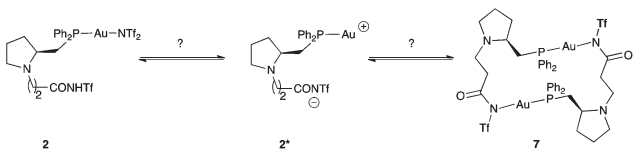


Fig. 3 Potential decomplexation of complexes **2** and **7** to give the same cationic gold intermediate **2***.

X-ligand prior to complexation with the substrate. Our design of complexes **2** and **7** should generate the same cationic species on dissociation of the X-ligand, as shown in Fig. 3. If the standard mechanistic proposal holds, then cationic gold **2***, formed from either **2** or **7**, should lead to identical results, if **2*** is the sole catalytic species.

The alkynyl substrate **13** was treated with two different complexes **2** and **7** and both showed similar catalytic activities with respect to the product, the yield and the rate. However, the resulting cyclopentane **12** had opposite optical rotations ($[\alpha]_D$: −3.2° with catalyst **2** and 3.2° with catalyst **7**). Entries 11–13 show that the thermal cycloisomerisation is not favourable, but proceeds in very poor yields to cyclopentane **12**. To rule out any organocatalytic activity of the ligand, either *via* the

corresponding iminium derived from the condensation of ligand **15** with ketones **11** or through H-bonding to either carbonyl, a test reaction was performed with the sole ligand **15** present. No cycloisomerisation was observed, even upon heating (Table 1, entries 14 and 15). The role of ligand metathesis and the influence of the chiral coordination sphere of the gold complex were also investigated by treating the alkyne with a mixture of triphenylphosphine bis-triflic amide gold complex **10** in the presence of either ligand **15** or L-proline (Table 1, entries 17–21). Surprisingly, and despite similar reactivity between our chiral gold complexes and the standard bis-triflic amide complex, the reaction did not proceed and starting material was recovered. This not only rules out any ligand metathesis, but also a potential weak interaction of the free ligand with any of the intermediates involved. These results also suggest that excess ligand suppresses any catalytic activity of the gold(I) complex. Though they do not preclude the intervention of a different cationic gold species, they clearly indicate the involvement of multiple intermediates in the catalysis of the isomerisation, including a possible tricoordinate gold intermediate. These results have prompted us to investigate the dynamic equilibration of gold amides in solution by contrasting the covalent radii of the complexes in the solid state with those obtained in solution using DOSY and freezing point depression experiments.

DOSY methodology

Diffusion ordered spectroscopy (DOSY) is a powerful technique for investigating the solution state assembly properties of molecules.[27–29] The technique relies upon measuring the attenuation of an NMR signal, during the application of pulsed magnetic field gradients, caused by incoherent sample motion, such as translational diffusion. Fitting this signal attenuation allows the transitional diffusion coefficient to be determined, thereby accessing information on effective molecular size in solution.[30]

Hydrodynamic radii were calculated from the Stokes–Einstein equation: $D = kT/(6\pi\eta r)$, where η represents the viscosity of the solution (taken to be the same as $CHCl_3$ at 25 °C).[29] Strictly, the Stokes–Einstein equation assumes that the diffusing particle is a hard sphere, and includes any solvation effects, therefore the radii obtained are guides to the true hydrodynamic size in solution. The results are compiled in Table 1.

Table 3 Results for the DOSY experiments

Entry	Compound	Diffusion coefficient D [10^{-10} m^2 s^{-1}]	Hydrodynamic radius r_H [Å]
1	**7**	3.2	12.6
2	**6a**	4.4	9.0
3	**5a**/**5b**	3.7	10.9
4	**15**	4.4	9.2
5	**16**	3.6	11.2
6	**1**	3.5	11.5
7	**2**	3.5	11.5

Interestingly, no signals for free ligands are observed in any of the experiments. The DOSY results for complex **5a**/**5b** (Table 3, entry 3) are consistent with a potential monomer–dimer equilibrium on the time scale of the diffusion measurement (10^2 ms) given that this molecule shows a larger diffusion coefficient than that of dimer **7**, but a smaller coefficient than that of monomer **6a** (Table 3, entry 2). As expected, the hydrodynamic radius of free ligand **15** (Scheme 5) is smaller than that of dimeric complex **7**. The radius of free ligand **16** (Scheme 5) however is larger than its complexed form **6a** as **16** has more conformational flexibility than the complex which has necessarily restricted bond rotations. This clearly indicates the lack of decomplexation of the X-side of the complex on the time-frame of the measurements, as the subsequent cationic gold species would have a radius similar or greater to that of free ligand **16**. Gold chlorides are stable in solution and do not decomplex to form cationic gold unless a co-catalyst is used, usually silver(I) salts. Interestingly, gold chloride **15** and gold bis-triflic amide **2** have a similar hydrodynamic radius and this confirms that **2** has a smaller radius than the dimeric version in solution which does not dissociate to a monomeric species. This also suggests that decomplexation of the bis-triflic amide residue and subsequent dimerisation to **7** were not observed at that concentration.

Freezing point depressions

Freezing point depression was chosen to examine and provide more evidence pertaining to the nature of gold amide complexes in solution. Freezing point depression, ΔT_f, can be used to evaluate the number of the solute particles through the van't Hoff factor i ($\Delta T_f = K_f m i$), and to determine the oligomeric state of the complex from the colligative property of the solution.

We found that complexes **6** and **7** were freely soluble in 1,2-dibromoethane, which has a convenient freezing point and a high cryoscopic constant (K_f = 12.5 K mol^{-1} kg^{-1}]. The results of the freezing point depressions are compiled in Table 4. Of note, data could not be collected for complex **5a**/**5b** as it could not be dissolved in the required solvent.

The results of these colligative experiments are consistent with the conclusions drawn from the DOSY experiments, in spite of a different dielectric constant for both solvents ($Br_2C_2H_4$: ε_r = 10.5, $CDCl_3$: ε_r = 4.8 at 293 K). In solution, the complex mixture **6a**/**6b** is predominantly a monomer contrary to its solid state which is the dimeric form **6b**. Complex **7** is indeed dimeric in both solvent and in the solid state.

Table 4 Freezing point depressions of gold amide complexes

Compounds	Expected ΔT_f (°C)	Observed ΔT_f (°C)
7	Dimer: 0.138 Monomer: 0.275	0.133
6a	Dimer **6b**: 0.214 Monomer **6a**: 0.428	0.433

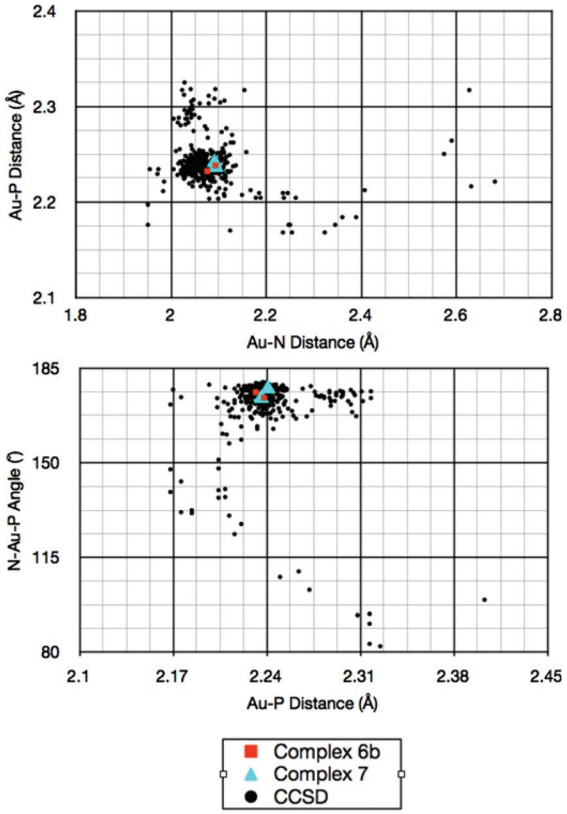


Fig. 4 Comparative graphs between angles and distances around the Au(I) centre.

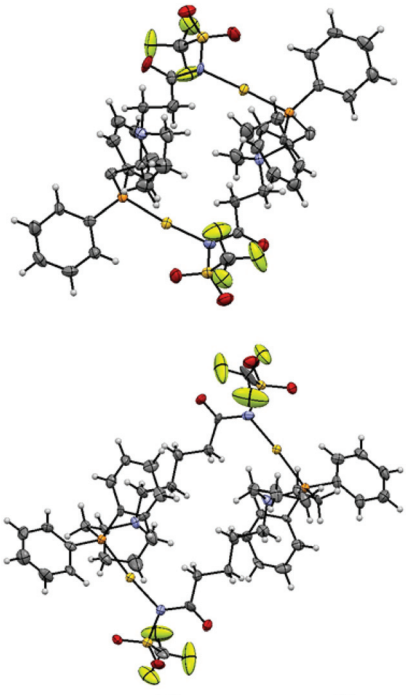


Fig. 5 Single crystal X-ray structures of complexes **6b** (top) and **7** (bottom). Selected bond lengths (Å) and angles (°): **6b** Au(1)–N(1) 2.094(8), Au(1)–P(1) 2.236(3), N(1)–Au(1)–P(1) 173.9(2), Au(2)–N(2) 2.091(7), Au(2)–P(2) 2.241(2), N(2)–Au(2)–P(2) 177.4(2), Au–Au 6.613, longest dimension 18.803; **7** Au(1)–N(1) 2.076(9), Au(1)–P(1) 2.232(2), N(1)–Au(1)–P(1) 176.1(4), Au(2)–N(2) 2.093(9), Au(2)–P(2) 2.238(3), N(2)–Au(2)–P(2) 174.1(4), Au–Au 9.077, longest dimension 20.255.

X-ray diffraction studies

Compounds **6b** and **7** both yielded crystals that were suitable for X-ray diffraction studies to augment our solution-phase experiments (Fig. 4). In both cases, full structural data are included in the ESI.† The molecular structures of these complexes all contain a two-coordinate Au centre with unexceptional Au–N and Au–P distances and linear coordination irrespective of the state of molecularity in the crystal (Fig. 5).

Amongst the 396 structures from the CCSD that have this coordination sphere composition, all are linear, with conventional distances except those where the system is particularly structurally constrained. Additionally, the amide nitrogen is invariably planar.

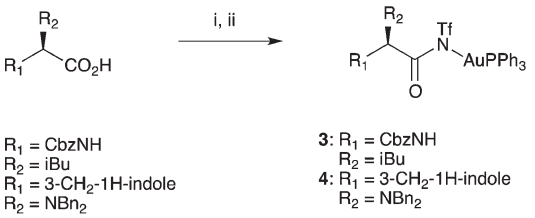
Interestingly the sequence of compounds **5**, **6** and **7** contains chains homologated by one CH_2 unit sequentially. **6** and **7** are both dimers, presumably because the strain required to form a mononuclear linear-coordinate Au complex from the corresponding bidentate ligands is too high. Interestingly, solution of poor data from a crystal of **5** showed that it is polymeric in the solid state and subject to high levels of disorder.

Of note, the crystal structures are composed of the units bound by F···H and O···H intermolecular bonds, leading to highly porous, layered structures. There is also no metal–metal interaction present in the solid state.

Synthesis of complexes 1–7

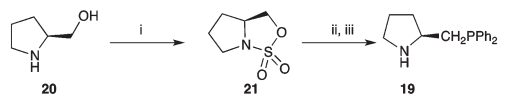
Complexes **3** and **4** were synthesised from protected amino acids Leucine and Tryptophan (Scheme 3). Carboxylic acids **17**[31] and **18** were interconverted into the corresponding *N*-triflic amide by treatment with EDC. Gold complexes **3** and **4** were then subsequently obtained by treating triphenylphosphine gold chloride with the corresponding silver amide salt generated *in situ*. The complexes were obtained as a mixture of rotamers (**3:** [7 : 3], **4:** [10 : 1]).

Complexes **1**, **2**, **5–7** all feature the same proline core **19**. Phosphine **19** was synthesised from prolinol **20** (Scheme 4). The aminol was activated as its cyclic sulfamidate **21**[32] and treated with $LiPPh_2$, followed by hydrolysis of the resulting sulfamic acid under oxygen free conditions to avoid any oxidation to the corresponding phosphine oxide. The ligands **15**, **16** and **22** were synthesised by nucleophilic substitution of the *N*-proline with the corresponding alkyl bromides (Scheme 5). The acid obtained after saponification of the methyl ester was then converted to the corresponding *N*-triflic alkanamides **15**, **16** and **22**. Ligand metathesis of the silver amide salt generated *in situ* with dimethylsulfide gold chloride gave different complexes depending on the length of the side chain. Both monomer **5a** and **6a** and dimer **6b** were observed for n = 3,4 (but solely the dimer in the solid state **6b**, as mentioned



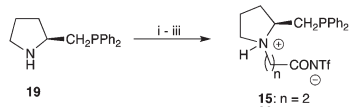
Reagents. (i) $TfNH_2$, EDC, HOBt, CH_2Cl_2 (53% from **17**, 73% from **18**); (ii) Ph_3PAuCl, Ag_2CO_3, CH_2Cl_2, quant.

Scheme 3 Synthesis of triphenylphosphine gold amides.



Reagents: i) SO_2Cl_2, Et_3N, CH_2Cl_2, 30%; (ii) PPh_3, Li, THF, 91%; (iii) Deoxygenated HCl (32%), 100 °C, 17 h, 65%.

Scheme 4 Synthesis of the core pyrrolidine precursor.



Reagents. (i) $BrC_nH_{2n}CO_2Me$, Et_3N, CH_2Cl_2, (n = 2: 47%, n = 3: 47%, n = 4: 65%); (ii) NaOH, H_2O, MeOH, (n = 2: quant., n = 3: quant., n = 4: 93%); (iii) $TfNH_2$, HOBt, EDC, CH_2Cl_2, (n = 2: 49%, n = 3: 46%, n = 4: 72%).

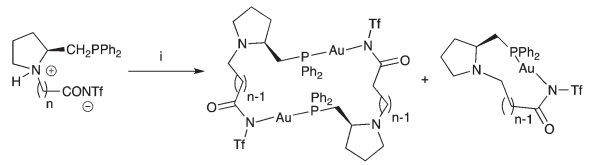
Scheme 5 Synthesis of the bidentate ligands.

earlier) (Scheme 6). In contrast, the sole dimer **7** was observed for $n = 2$.

The introduction of L-ligand **15** was achieved by treating dimethylsulfide gold chloride in the absence of Ag(I). The corresponding complex **1** was then converted to its bis-triflic amide complex **2** after ligand metathesis with silver bis-triflic amide (Scheme 7).

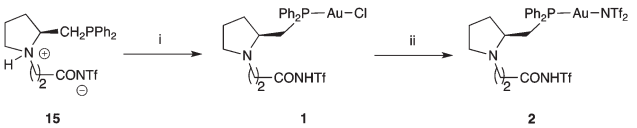
Conclusions

It has been demonstrated that the catalytic activity of gold amide complexes is highly dependent on the nature of the substitution around the *N*-linkage and that the widely accepted cationic nature of organogold complexes in solution cannot be generalized to *N*-triflic alkanamide gold complexes. We have shown by DOSY NMR studies and freezing point depression studies that dimeric complex **6b** in the solid state equilibrates to monomer **6b** in solution, suggesting that an amide X-ligand is indeed labile in solution. We have also observed that complexes **2** and **7** featuring the same L-ligand but different X-ligands gave opposite optical rotations for the cycloisomerisation of alkynes. The fact that ligand **15** does not display any organocatalytic activity and that it inhibited complex **10** suggests that the observed enantio-discrimination stems from the complexation of the alkynyl substrate with the gold amides



Reagents. (i) Me_2SAuCl, Ag_2CO_3, CH_2Cl_2, (n = 2-4: quant.).

Scheme 6 Synthesis of complexes **5–7**.



Reagents. (i) Me_2SAuCl, CH_2Cl_2, 94%; (ii) Tf_2NH, Ag_2CO_3, CH_2Cl_2, 80%.

Scheme 7 Synthesis of complexes **1** and **2** with modified L-ligand **15**.

prior to the decomplexation of the X-ligand to give the formation of a cationic gold species.

Experimental section

Methods and materials

Reagent grade solvents were dried by the standard procedures and were freshly distilled prior to use. IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One spectrophotometer. Mass spectra were recorded on VG Autospec Magnetic Sector MS and Bruker Daltonic FT-ICR-MS Apex III instruments. NMR spectra were recorded on either a Varian VNMRS 400 or a VNMRS 500 instrument. Chemical shifts were referenced to residual solvent resonances or external 85% H_3PO_4 in ^1H and ^{31}P NMR spectra as appropriate. The units for the reported $[\alpha]_D$ values are: $[\alpha]$ = deg cm^3 g^{-1} dm^{-1}, c = cgd m^{-3}. Flash column chromatography was carried out using Apollo Zeoprep 60 Hyd 35–70 micron silica gel. The freezing point depressions were measured with an AutoTherm II Plus thermometer in high-resolution mode (DIN standard). The data were collected with the Metter Toledo program. A platinum resistance thermometer probe (no. 515–131) was used with the following errors: 0.001 °C for 10.048 °C −0.004 °C for 5.041 °C.

Syntheses

Methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}-propanoate. A solution of methyl-3-bromopropionate (1.55 g, 9.28 mmol, 1.01 mL) in dichloromethane (8.0 mL) was added dropwise to a solution of triethylamine (1.88 g, 18.57 mmol, 2.61 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (2.50 g, 9.28 mmol) in dichloromethane (27 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water–dichloromethane (1 : 1, 200 mL). The organic phase was washed with water (100 mL), brine (100 mL) and then dried over sodium sulfate, filtered and

concentrated under reduced pressure. Purification by column chromatography (methanol–dichloromethane, [5 : 95]) afforded the title compound as a yellow viscous oil (1.57 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50–7.39 (4H, m, Ar), 7.37–7.28 (6H, m, Ar), 3.66 (3H, s, 9-H), 3.19–3.03 (2H, m, 5, 6-H), 2.54 (1H, dt, J = 3.3, 13.3, 4-H), 2.49–2.29 (4H, m, 6, 7-H), 2.15–2.06 (1H, m, 5-H), 2.06–1.91 (2H, m, 1, 3-H), 1.83–1.53 (3H, m, 3, 4-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 172.7 (s, 8-C), 139.3 (d, J = 12.1, Ar), 138.5 (d, J = 13.3, Ar), 133.0 (d, J = 19.3, Ar), 132.6 (d, J = 18.7, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 62.1 (d, J = 19.3, 2-CH), 53.4 (d, J = 0.8, 5-CH_2), 51.5 (s, 9-CH_3), 49.1 (s, 6-CH_2), 33.6 (d, J = 13.3, 1-CH_2), 33.5 (s, 7-CH_2), 31.7 (d, J = 7.8, 3-CH_2), 22.1 (d, J = 0.6, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −21.20. IR (diamond, ν_{MAX}, cm^{-1}) 2961, 2802 (CH_3O st), 1735 (C═O st), 1433 (H–C–H st as), 1175 (C–O st as). $[\alpha]_D^{26}$ = −78.2 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{21}H_{27}NO_2P$ Found: 356.1778 error [ppm]: −1.28 Calculated: 356.1774.

3-{(2*S*)-2-[(Diphenylphosphino)methyl]pyrrolidin-1-yl}propanoic acid. A solution of 34.3 mL of the 1 N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]-pyrrolidin-1-yl}propanoate (0.50 g, 1.41 mmol) in methanol (22.85 mL, 0.062 M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (3.5 mL). The resulting solution was lyophilized to yield the crude product which was then dissolved in methanol. Any insoluble salts were removed by filtration. The resultant solution was concentrated under reduced pressure to give the corresponding compound as a yellow and cloudy viscous oil (0.57 g, quantitative). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (1H, br s, OH), 7.40 (10H, m, Ar), 3.70–3.80 (1H, m, 5-H), 3.61–3.49 (1H, m, 7-H), 3.06–2.72 (6H, m, 1, 6, 7, 5-H), 2.64 (1H, t, J = 12.1, 1-H), 2.24–1.82 (m, 4H, 3, 4-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.2 (s, 8-C), 136.8 (d, J = 11.3, Ar), 136.1 (d, J = 12.7, Ar), 133.0 (d, J = 20.2, Ar), 132.5 (d, J = 19.2, Ar), 129.6 (s, Ar), 129.1 (s, Ar), 128.9 (d, J = 7.3, Ar), 128.7 (d, J = 6.9, Ar), 66.9 (d, J = 23.2, 2-CH), 52.8 (s, 5-CH_2), 49.4 (s, 7-CH_2), 31.1 (s, 6-CH_2), 30.5 (d, J = 7.4, 3-CH_2), 29.6 (d, J = 16.2, 1-CH_2), 21.7 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −20.61 (s), 30.43 (s, P═O, 5%). IR (diamond, ν_{MAX}, cm^{-1}) 2956, 2547 (HO st), 1720 (C═O st), 1432 (H–C–H st as). $[\alpha]_D^{26}$ = −40.0 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{20}H_{25}NO_2P$ Found: 342.1608 m/z error [ppm]: 2.86 Calculated: 342.1617 m/z.

(3-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-propanoyl)((trifluoromethyl)sulfonyl)amide (15). 3-{(2*S*)-2-[(Diphenylphosphino)methyl]pyrrolidin-1-yl}propanoic acid (0.50 g, 1.46 mmol), triflic amine (0.218 g, 1.46 mmol) and HOBt·H_2O (0.224 g, 1.46 mmol) were dissolved in dichloromethane (3.85 mL) and cooled to 0 °C. EDC (0.233 g, 1.50 mmol) was added and the mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in 20 mL of dichloromethane and washed with 1 M citric acid (20 mL), saturated sodium bicarbonate (20 mL), brine (20 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol–dichloromethane, [5 : 95]) afforded the title compound as a colourless solid (0.34 g, 49%). ^{1}H NMR (500 MHz, DMSO) δ = 7.55–7.32 (10H, m, Ar), 3.75–3.45 (2H, m, 5, 6-H), 3.22 (1H, s, 2-H), 3.11–2.89 (3H, m, 1, 5, 6-H), 2.55–2.45 (2H, m, 7-H), 2.28 (1H, t, J = 12.1, 1-H), 2.15–2.03 (1H, m, 3-H), 1.94–1.77 (2H, m, 4-H), 1.74–1.60 (1H, m, 3-H). ^{13}C NMR (126 MHz, DMSO) δ = 174.3 (s, 8-C), 137.3 (d, J = 12.2, Ar), 136.2 (d, J = 13.2, Ar), 132.7 (d, J = 19.9, Ar), 132.4 (d, J = 19.6, Ar), 129.2 (d, J = 33.7, Ar), 128.8 (d, J = 7.1, Ar), 128.6 (d, J = 7.0, Ar), 124.1 (s, 9-CF), 121.5 (s, 9-CF), 118.9 (s, 9-CF), 116.4 (s, 9-CF), 66.1 (d, J = 23.5, 2-CH), 52.8 (s, 5-CH_2), 49.6 (s, 6-CH_2), 34.3 (s, 7-CH_2), 30.1 (s, 3-CH_2), 28.9 (d, J = 13.0, 1-CH_2), 21.4 (s, 4-CH_2). ^{31}P NMR (162 MHz, DMSO) δ = −21.76 (s). ^{19}F NMR (376 MHz, DMSO) δ = −77.71 (s). M.p.: 153–155 °C. IR (diamond, ν_{MAX}, cm^{-1}) 3052, 2967 (NH st), 2192 (Ar comb), 1598 (C═O st amide), 1431 (H–C–H st as), 1176 (S–O st as), 1123 (S–O st sy). $[\alpha]_D^{26}$ = −27.7 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{21}H_{24}F_3N_2NaO_3PS$ Found: 495.1117 m/z error [ppm]: −5.50 Calculated: 495.1090 m/z.

X-Ray: see the appendix for complex **15** (recrystallised from chloroform).

(3-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-propanoyl)((trifluoromethyl)sulfonyl)amide gold chloride (1). (3-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)propanoyl)((trifluoromethyl)sulfonyl)amide (50 mg, 0.106 mmol) was dissolved in dry dichloromethane (1 mL) under an atmosphere of nitrogen. Dimethyl sulfide gold chloride (31 mg, 0.106 mmol) was added to one portion and the resulting mixture was stirred for 3 h. Concentration of the reaction mixture under reduced pressure afforded the title compound as a colourless solid (70 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (2H, dd, J = 7.1, 13.6, Ar), 7.80 (2H, dd, J = 7.1, 13.4, Ar), 7.59–7.42 (6H, m, Ar), 4.26 (1H, m, 5-H), 3.86–3.58 (2H, m, 6-H), 3.53–3.37 (2H, m, 1-H), 3.02–2.90 (2H, m, 5, 6-H), 2.83–2.55 (2H, m, 7-H), 2.19–1.91 (3H, m, 3, 4-H), 1.80–1.67 (1H, m, 3-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6 (s, 8-C), 134.1 (d, J = 14.3, Ar), 133.1 (d, J = 13.6, Ar), 132.6 (dd, J = 2.1, 52.4, Ar), 129.5 (dd, J = 6.8, 12.1, Ar), 128.6 (d, J = 63.1, Ar), 127.9 (d, J = 61.7, Ar), 124.12 (s, 9-CF), 121.5 (s, 9-CF), 119.0 (s, 9-CF), 116.4 (s, 9-CF), 67.7 (s, 2-CH), 54.6 (s, 5-CH_2), 52.3 (s, 6-CH_2), 34.5 (s, 7-CH_2), 30.4 (s, 3-CH_2), 29.1 (d, J = 38.9, 1-CH_2), 21.9 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.38 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −78.34 (s). Compound decomposed at 128–130 °C. IR (diamond, ν_{MAX}, cm^{-1}) 3055 (NH st), 2191 (Ar comb), 1610 (C═O st amide), 1437 (H–C–H st as), 1173 (S–O st as), 1124 (S–O st sy). $[\alpha]_D^{26}$ = −12.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{21}H_{24}AuClF_3N_2NaO_3PS$ Found: 727.0440 m/z error [ppm]: 0.48 Calculated: 727.0444 m/z.

(3-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-propanoyl)((trifluoromethyl)sulfonyl)amide gold bis-triflic amide (2). A solution of gold diphenylphosphine chloride (65.2 mg, 0.092 mmol) in dichloromethane (0.31 mL) was added to a premixed (5 min) solution of bis-triflic amide (26 mg, 0.092 mmol) and silver carbonate (25.5 mg,

0.092 mmol) in dry dichloromethane (2 mL) under an inert atmosphere. The resulting mixture was stirred for 2 h excluding light. The mixture was filtered through Celite and concentrated under reduced pressure to give the title compound as an off white solid (70.5 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.17–6.96 (10H, m, Ar), 4.33–2.89 (9H, m, 1, 5, 6, 7-H), 2.22–1.75 (3H, m, 3, 4-H), 1.47–1.21 (1H, m, 3-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 174.8 (s, C-8), 134.9 (d, J = 14.0, Ar), 133.8 (s, Ar), 132.2 (s, Ar), 131.7 (d, J = 12.2, Ar), 130.0 (s, Ar), 129.6 (s, Ar), 129.4 (d, J = 11.7, Ar), 123.4 (s, CF), 120.9 (s, CF), 118.3 (s, CF), 115.7 (s, CF), 64.4 (s, 2-CH), 52.8 (s, 5-CH_2), 44.9 (s, 6-CH_2), 29.5, 29.1 (s, 1, 3, 7-CH_2), 20.8 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 26.80 (s). ^{19}F NMR (376 MHz, $CDCl_3$) δ = −76.56 (s), −78.68 (s). Compound decomposed at 109–111 °C. IR (diamond, ν_{MAX}, cm^{-1}) 2178 (Ar comb), 1669 (C═O st amide), 1439 (H–C–H st as), 1178 (S–O st as), 1128 (S–O st sy). $[\alpha]_D^{26}$ = −23.6 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{23}H_{24}$ $AuF_9N_3O_7PS_3$ Found: N/A Calculated: 949.5735.

Bidentate gold(I) complex (7)

(3-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-propanoyl) ((trifluoromethyl)sulfonyl)amide. (100 mg, 0.212 mmol) was dissolved in dry dichloromethane (2.1 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (62 mg, 0.212 mmol) was added to one portion and the mixture was stirred for 15 min. The silver carbonate (58 mg, 0.212 mmol) was added to one portion and the resultant mixture stirred overnight. The reaction mixture was filtered through Celite and concentrated under reduced pressure to give the title compound as a yellow solid (139 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91–7.37 (10H m, Ar), 3.36–1.23 (13H m, 1–7-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 176.6 (s, 8-C), 133.6 (s, Ar), 133.0 (s, Ar), 132.2 (s, Ar), 129.9 (s, Ar), 129.4 (s, Ar), 129.3 (s, Ar), 125.4 (s, 9-CF), 122.1 (s, 9-CF), 118.7 (s, 9-CF), 115.5 (s, 9-CF), 61.8 (s, 2-CH), 53.4 (s, 5-CH_2), 50.04 (s, 6-CH_2), 37.4 (s, 7-CH_2), 33.2 (s, 3-CH_2), 31.9 (s, 1-CH_2), 22.8 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 21.92 (s), 20.81 (s). Compound decomposed at 125–126 °C. IR (diamond, ν_{MAX}, cm^{-1}) 2962 (NH st), 2168 (Ar comb), 1683 (C═O st amide), 1437 (H–C–H st as), 1177 (S–O st as), 1121 (S–O st sy). $[\alpha]_D^{24}$ = −21.2 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{42}H_{47}$ $Au_2F_6N_4O_6P_2S_2$ Found: 1337.1704 m/z error [ppm]: −4.61 Calculated: 1337.1704 m/z.

X-Ray: available see the appendix (by slow diffusion of dichloromethane into benzene).

(*S*)-Methyl 5-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-pentanoate. A solution of methyl 5-bromopentanoate (0.36 g, 1.86 mmol, 0.27 mL) in dichloromethane (1.64 mL) was added dropwise to a solution of triethylamine (0.38 g, 3.71 mmol, 0.52 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (0.500 g, 1.86 mmol) in dichloromethane (5.46 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water–dichloromethane (1 : 1, 40 mL). The crude residue was extracted with dichloromethane (20 mL), the organic phase was washed with water (20 mL), brine (20 mL) and then dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (methanol–dichloromethane, [5 : 95]) afforded the title compound as a colourless viscous oil (1.57 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55–7.27 (10H, m, Ar), 3.66 (3H, s, 11-H), 3.21 (1H, s, 5-H), 2.82 (1H, m, 5-H), 2.54 (1H, dt, J = 3.1, 13.2, 3-H), 2.40 (1H, s, 2-H), 2.33–2.27 (2H, m, 9-H), 2.21–2.04 (3H, m, 3, 6-H), 2.04–1.96 (1H, m, 1-H), 1.83 (1H, m, 4-H), 1.74–1.45 (5H, m, 4, 7, 8-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.9 (s, 10-C), 133.09 (s, Ar), 132.94 (s, Ar), 132.62 (s, Ar), 132.47 (s, Ar), 128.82 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 62.8 (s, 2-CH), 53.6 (s, 6-CH_2), 53.5 (s, 5-CH_2), 51.5 (s, 11-CH_3), 33.8 (s, 9-CH_2), 33.2 (s, 3-CH_2), 31.6 (s, 1-CH_2), 27.6 (s, 7-CH_2), 22.9 (s, 8-CH_2), 22.1 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −20.82 (s). IR (diamond, ν_{MAX}, cm^{-1}) 2945, 2788 (CH_3O st), 1734 (C═O st), 1433 (H–C–H st as), 1169 (C–O st as). $[\alpha]_D^{24}$ = −46.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{23}H_{31}NO_2P$ Found: 384.2078 error [ppm]: 2.43 Calculated: 384.2087.

(*S*)-5-(2-((Diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid. A solution of 27.5 mL of the 1 N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}pentanoate (0.41 g, 1.11 mmol) in methanol (18.5 mL, 0.062 M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (2.8 mL). The resulting solution was lyophilized to yield the crude product which was then dissolved in methanol. Any insoluble salts were removed by filtration. The resultant solution was concentrated under reduced pressure to give the corresponding compound as a colourless viscous oil (0.38 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 11.94–11.20 (1H, br s, OH), 7.59–7.30 (10H, m, Ar), 3.84 (1H, s, 5-H), 3.26 (1H, s, 6-H), 3.03–2.56 (5H, m, 1, 2, 5, 6-H), 2.34 (2 H, t, J = 6.7, 9-H), 2.20 (2 H, s, 3, 4-H), 2.04 (1 H, s, 3-H), 1.93 (2 H, s, 4, 7-H), 1.74–1.52 (3 H, m, 7, 8-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 175.6 (s, 10-C), 136.4 (s, Ar), 133.2 (d, J = 14.26, Ar), 132.5 (s, Ar), 129.7 (s, Ar), 129.1 (s, Ar), 128.9 (s, Ar), 128.7 (s, Ar), 67.1 (s, 2-CH), 52.9 (s, 5, 6-CH_2), 33.1 (s, 9-CH_2), 30.6 (s, 3-CH_2), 29.8 (s, 1-CH_2), 24.4 (s, 7-CH_2), 22.0 (s, 8-CH_2), 21.7 (s, 4-CH_2). IR (diamond, ν_{MAX}, cm^{-1}) 2945, 2546 (HO st), 1720 (C═O st), 1432 (H–C–H st as), 1169 (C–O st as). $[\alpha]_D^{24}$ = −44.1 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{22}H_{29}NO_2P$ Found: 370.1921 error [ppm]: 2.57 Calculated: 370.1930.

(5-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)pentanoyl)((trifluoromethyl)sulfonyl)amide (16). (*S*)-5-(2-((Diphenylphosphino)methyl)pyrrolidin-1-yl)pentanoic acid (0.300 g, 0.81 mmol), triflic amine (0.121 g, 0.81 mmol) and HOBt·H_2O (0.125 g, 0.14 mmol) were dissolved in dichloromethane (2.15 mL) and cooled to 0 °C. EDC (0.140 g, 0.83 mmol) was added and the mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in 15 mL of dichloromethane and washed with 1 M citric acid (15 mL), saturated sodium bicarbonate (15 mL), brine (15 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol–

dichloromethane, [5 : 95]) afforded the title compound as a white solid (0.268 g, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.56–7.30 (10H, m, Ar), 3.98 (1H, s, 5-H), 3.40 (1H, s, 6-H), 2.95 (1 H, s, 2-H), 2.82 (2 H, m, 1, 5-H), 2.63–2.38 (4 H, m, 1, 6, 9-H), 2.29–2.16 (2 H, m, 3, 4-H), 2.08–1.86 (2 H, m, 3, 4-H), 1.79 (1 H, s, 7-H), 1.71–1.52 (3 H, m, 7, 8H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 181.0 (s, 10-C), 136.7 (d, J = 11.4, Ar), 136.4 (d, J = 10.9, Ar), 133.1 (d, J = 20.1, Ar), 132.4 (d, J = 19.1, Ar), 129.7 (s, Ar), 129.1 (s, Ar), 129.0 (d, J = 7.2, Ar), 128.7 (d, J = 6.6, Ar), 124.2 (s, 10-CF), 121.7 (s, 10-CF), 119.1 (s, 10-CF), 68.4 (d, J = 23.9, 2-CH), 54.8 (s, 6-CH_2), 53.8 (s, 5-CH_2), 37.5 (s, 9-CH_2), 30.6 (d, J = 7.1, 3-CH_2), 29.8 (d, J = 15.1, 1-CH_2), 24.7 (s, 7-CH_2), 22.6 (s, 8-CH_2), 21.7 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −20.38 (s). M.p.: 147–149 °C. IR (diamond, ν_{MAX}, cm^{-1}) 2962 (NH st), 2192 (Ar comb), 1602 (C═O st amide), 1431 (H–C–H st as), 1168 (S–O st as), 1126 (S–O st sy). $[\alpha]_D^{24}$ = −21.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{23}H_{28}F_3N_2NaO_3PS$ Calculated: 523.1403 error [ppm]: 2.11 Found: 523.1392.

Complexes (6a)/(6b)

(5-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-pentanoyl)((trifluoromethyl)sulfonyl)amide (100 mg, 0.199 mmol) was dissolved in dry dichloromethane (2.0 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (58.9 mg, 0.199 mmol) was added to one portion and the mixture was stirred for 15 min. The silver carbonate (55.1 mg, 0.199 mmol) was added to one portion and the resultant mixture stirred overnight. The reaction mixture was filtered through Celite and concentrated under reduced pressure to give the title compound as a yellow solid (138.7 mg, quantitative). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.83–7.69 (4H, m, Ar), 7.57–7.45 (6H, m, Ar), 3.12–3.04 (1H, m, 6-H), 2.97–2.63 (5H, m, 2, 3, 5, 9-H), 2.57–2.47 (1H, m, 9-H), 2.33–2.20 (2H, m, 6–8-H), 2.19–2.10 (1H, m, 5-H), 1.90–1.45 (6H, m, 1, 4, 8, 7-H), 1.35–1.24 (1H, m, 1-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.8 (s, 10-C), 133.1 (d, J = 12.9, Ar), 133.5 (d, J = 13.9, Ar), 132.1 (d, J = 22.7, Ar), 129.5 (s, Ar), 129.4 (s, Ar), 129.4 (s, Ar), 122.0 (s, 11-CF), 61.6 (s, 2-CH), 53.3 (s, 6-CH_2), 51.6 (s, 5-CH_2), 40.2 (s, 9-CH_2), 32.3 (d, J = 40.9, 3-CH_2), 31.3 (s, 1-CH_2), 26.4 (s, 7-CH_2), 23.9 (s, 8-CH_2), 22.3 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 16.41 (s) corresponding as monomer **6a**. IR (diamond, ν_{MAX}, cm^{-1}) 2925, 2798 (NH st), 2168 (Ar comb), 1694 (C═O st amide), 1436 (H–C–H st as), 1176 (S–O st as), 1123 (S–O st sy). Compound decomposed at 93–95 °C. $[\alpha]_D^{24}$ = −22.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{23}H_{28}AuF_3N_2NaO_3PS$ Found: 719.0962 error [ppm]: 0.52 Calculated: 719.0966 Acc. Mass (FAB): $C_{46}H_{54}Au_2F_6N_4NaO_6P_2S_2$ Found: 1415.2089 error [ppm]: −0.12 Calculated: 1415.2087.

X-Ray: dimer **6b** (recrystallised by slow diffusion of dichloromethane into *n*-heptane).

(*S*)-Methyl 4-(2-((diphenylphosphino)methyl)pyrrolidin-1-yl)-butanoate. A solution of methyl 5-bromobutanoate (0.273 g, 1.51 mmol) in dichloromethane (1.32 mL) was added dropwise to a solution of triethylamine (0.304 g, 3.01 mmol, 0.42 mL) and (2*S*)-2-[(diphenylphosphino)methyl]pyrrolidine (0.405 g, 1.51 mmol) in dichloromethane (3.1 mL). The resultant solution was stirred at 30 °C overnight. The reaction mixture was poured into water–dichloromethane (1 : 1, 32 mL). The crude residue was extracted with dichloromethane (16 mL), the organic phase was washed with water (16 mL), brine (16 mL) and then dried over sodium sulfate, filtered and concentrated under reduced pressure. Purification by column chromatography (methanol–dichloromethane, [5 : 95]) afforded the title compound as a colourless viscous oil (0.264 g, 47%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51–7.40 (4H, m, Ar), 7.38–7.28 (6H, m, Ar), 3.66 (3H, d, J = 1.3, 11-H), 3.19 (1H, s, 5-H), 2.80 (1 H, m, 6-H), 2.51 (1 H, d, J = 13.1, 1-H), 2.46–2.22 (3H, m, 2, 8-H), 2.14 (3H, s, 1, 5, 6-H), 2.03–1.94 (1H, m, 3-H), 1.86–1.57 (5H, m, 3, 4, 7-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 173.8 (s, 10-C), 139.2 (s, Ar), 138.4 (s, Ar), 133.0 (d, J = 19.5, Ar), 132.6 (d, J = 18.7, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 62.5 (s, 2-CH), 53.4 (s, 5-CH_2), 53.1 (s, 6-CH_2), 51.4 (s, 10-CH_3), 33.5 (s, 1-CH_2), 31.9 (s, 8-CH_2), 31.7 (d, J = 7.4, 3-CH_2), 23.6 (s, 7-CH_2), 22.2 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = −21.02 (s). IR (diamond, ν_{MAX}, cm^{-1}) 2949, 2791 (CH_3O st), 1733 (C═O st), 1433 (H–C–H st as), 1170 (C–O st as). Acc. Mass (FAB): $C_{22}H_{29}NO_2P$ Found: 370.1913 error [ppm]: 4.76 Calculated: 370.1930.

(*S*)-4-(2-((Diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid. A solution of 15.7 mL of the 1 N sodium hydroxide was added to methyl 3-{(2*S*)-2-[(diphenylphosphino)methyl]pyrrolidin-1-yl}butanoate (0.237 g, 0.64 mmol) in methanol (10.4 mL, 0.062 M). After stirring for 20 h at room temperature the reaction mixture was neutralized with 32% hydrochloric acid (1.7 mL). The resulting solution was lyophilized to yield the crude product which was then dissolved in methanol. Any insoluble salts were removed by filtration. The resultant solution was concentrated under reduced pressure to give the corresponding compound as a colourless oil (0.228 g, quantitative). ^{1}H NMR (500 MHz, CD_3OD) δ = 7.58–7.45 (4H, m, Ar), 7.44–7.35 (5H, m, Ar), 3.70–3.60 (1H, m, 5-H), 3.40–3.32 (1H, m, 6-H), 3.25–3.14 (1H, m, 2-H), 3.13–3.02 (1H, m, 5-H), 3.00–2.90 (1H, m, 6-H), 2.84 (1H, dd, J = 3.4, 13.3, 1-H), 2.48–2.35 (3H, m, 1, 8-H), 2.32–2.23 (1H, m, 3-H), 2.10–1.80 (5H, m, 3, 4, 7-H). ^{13}C NMR (126 MHz, CD_3OD) δ = 181.3 (s, 9-C), 138.8 (d, J = 11.5, Ar), 137.9 (d, J = 12.4, Ar), 134.3 (d, J = 20.2, Ar), 133.8 (d, J = 19.5, Ar), 130.8 (s, Ar), 130.4 (s, Ar) 130.1 (d, J = 7.3, Ar), 129.9 (d, J = 7.0, Ar), 67.4 (d, J = 21.9, 2-CH), 55.2 (s, 6-CH_2), 54.4 (s, 5-CH_2), 36.2 (s, 8-CH_2), 32.0 (d, J = 7.8, 3-CH_2), 31.5 (d, J = 15.8, 1-CH_2), 23.3 (s, 7-CH_2), 22.9 (s, 4-CH_2). ^{31}P NMR (162 MHz, CD_3OD) δ = −21.13 (s). IR (diamond, ν_{MAX}, cm^{-1}) 3307, 2541 (HO st), 1586 (C═O st), 1432 (H–C–H st as) 1154 (C–O st as). $[\alpha]_D^{23}$ = −13.9 (c = 1.0 in methanol). Acc. Mass (FAB): $C_{22}H_{29}NO_2P$ Found: 356.1768 error [ppm]: 1.76 Calculated: 356.1774.

(4-((2*S*)-2-((Diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)-butanoyl)((trifluoromethyl)sulfonyl)amide (22). (*S*)-5-(2-((Diphenylphosphino)methyl)pyrrolidin-1-yl)butanoic acid (0.233 g, 0.65 mmol), triflic amine (0.098 g, 0.65 mmol) and HOBt·H_2O (0.100 g, 0.65 mmol) were dissolved in dichloromethane (1.72 mL) and cooled to 0 °C. EDC (0.104 g,

0.67 mmol) was added and the mixture was stirred for 15 min at 0 °C and then at room temperature overnight. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in 10 mL of dichloromethane and washed with 1 M citric acid (10 mL), saturated sodium bicarbonate (10 mL), brine (10 mL) and dried over anhydrous magnesium sulfate; concentrated under reduced pressure. Purification by column chromatography (methanol–dichloromethane, [5 : 95], solid deposit) afforded the title compound as a white solid (0.145 g, 46%). ^{1}H NMR (500 MHz, DMSO) δ = 7.61–7.35 (10H, m, Ar), 3.58 (1H, s, 5-H), 3.45–3.37 (1H, m, 6-H), 3.20 (1H, s, 2-H), 3.09–3.02 (1H, m, 5-H), 2.99–2.84 (2H, m, 1, 6-H), 2.31–2.09 (4H, m, 1, 3, 8-H), 1.97–1.60 (5H, m, 3, 4, 7-H). ^{13}C NMR (126 MHz, DMSO) δ = 176.6 (s, 9-C), 137.3 (d, J = 12.1, Ar), 136.0 (d, J = 13.1, Ar), 132.7 (d, J = 20.0, Ar), 132.4 (d, J = 19.5, Ar), 129.4 (s, Ar), 129.1 (s, Ar), 128.8 (d, J = 7.2, Ar), 128.6 (d, J = 6.9, Ar), 124.3 (s, 10-CF), 121.7 (s, 10-CF), 119.1 (s, 10-CF), 116.5 (s, 10-CF), 65.7 (d, J = 21.9, 2-CH), 52.6 (s, 5-CH_2), 52.3 (s, 6-CH_2), 36.0 (s, 8-CH_2), 30.0 (d, J = 8.3, 3-CH_2), 28.7 (d, J = 14.3, 1-CH_2), 21.5 (s, 7-CH_2), 21.2 (s, 4-CH_2). ^{31}P NMR (162 MHz, DMSO) δ = −25.11 (1s). M.p.: 158–160 °C. IR (diamond, ν_{MAX}, cm^{-1}) 2967, 2554 (NH st), 2192 (Ar comb), 1645 (C═O st amide), 1434 (H–C–H st as), 1158 (S–O st as), 1134 (S–O st sy). $[\alpha]_D^{22}$ = −5.6 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{22}H_{26}F_3N_2NaO_3PS$ Calculated: 509.1246 error [ppm]: 0.31 Found: 509.1244.

Complexes (5a)/(5b)

The (4-((2*S*)-2-((diphenylphosphino)methyl)pyrrolidin-1-ium-1-yl)butanoyl)((trifluoromethyl)sulfonyl) amide (100 mg, 0.21 mmol) was dissolved in dry dichloromethane (2.1 mL) in a flame dried flask, under nitrogen. The dimethyl sulfide gold chloride (60.5 mg, 0.21 mmol) was added to one portion and the mixture was stirred for 15 min. The silver carbonate (56.7 mg, 0.21 mmol) was added to one portion and the resultant mixture stirred overnight. The reaction mixture was filtered through Celite and concentrated under reduced pressure to afford the title compound as a yellow solid (122 mg, quantitative w/w (monomer or dimer)). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.89–7.33 (10H m, Ar), 3.29–1.52 (15H m, 1–8-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 177.6 (s, 9-C), 133.5 (s, Ar), 133.0 (s, Ar), 132.2 (s, Ar), 132.0 (s, Ar), 131.0 (s, Ar), 129.9 (s, Ar), 129.4 (s, Ar), 129.4 (s, Ar), 129.0 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 121.9 (s, 10-CF), 119.3 (s, 10-CF), 116.6 (s, 10-CF), 62.1 (s, 2-CH), 53.6 (s, 5-CH_2), 52.9 (s, 6-CH_2), 33.7 (s, 1-CH_2), 33.4 (s, 8-CH_2), 32.0 (s, 3-CH_2), 24.0 (s, 7-CH_2), 22.7 (s, 4-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 23.06 (s), 21.55 (br, s), 19.68 (s). Compound decomposed at 109–111 °C. IR (diamond, ν_{MAX}, cm^{-1}) 2935 (NH st), 2168 (Ar comb), 1688 (C═O st amide), 1436 (H–C–H st as), 1177 (S–O st as), 1121 (S–O st sy). $[\alpha]_D^{20}$ = −37.7 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{22}H_{26}AuF_3N_2O_3PS$ Found: 683.1014 error [ppm]: −1.50 Calculated: 683.1014. Acc. Mass (FAB): $C_{44}H_{51}Au_2F_6N_4O_6P_2S_2$ Found: 1365.1874 error [ppm]: 5.91 Calculated: 1365.1955.

***N*,*N*-Dibenzyl-*N*[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide.** *N*,*N*-Dibenzyl-(*D*)-tryptophan **18** (0.152 g, 0.40 mmol), triflic amine (58.9 mg, 0.40 mmol) and HOBt·H_2O (60.5 mg, 0.40 mmol) were dissolved in dichloromethane (1.05 mL) at 0 °C. EDC (60.0 mg, 0.40 mmol) was added and the mixture stirred for 15 min and then at room temperature for a further 3 days. The precipitate was filtered off and the filtrate evaporated under reduced pressure. The residue was dissolved in 5 mL of ethyl acetate and washed with 1 M citric acid, saturated sodium bicarbonate, brine, dried over anhydrous magnesium sulphate, filtered and concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as a white solid (0.149 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.45 (1H, br s, NH), 7.37–6.82 (15H, m, Ar), 4.09–3.51 (6H, m, 12, 13, 3-H), 1.27 (1H, dd, J = 8.4, 15.0, 3-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 171.9 (s, 1-C) 136.3 (s, Ar), 129.1 (d, J = 18.25 Ar), 126.5 (s, Ar), 123.8 (s, Ar), 122.3 (s, Ar), 121.4 (s, Ar), 119.6 (s, Ar), 118.9 (s, Ar), 118.4 (s, Ar), 111.7 (s, Ar), 64.9 (s, 2-CH), 54.7 (s, 12, 13-CH_2), 29.7 (s, 3-CH_2). M.p.: 72–74 °C. IR (diamond, ν_{MAX}, cm^{-1}) 3403.21 (Ar NH st), 2919.69 (NH st), 2019.56 (Ar comb), 1619.39 (C═O st amide), 1179.12, 1180.95 (S–O st as), 1125.62 (S–O st sy). $[\alpha]_D^{21}$ = 39.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{26}H_{24}F_3N_3O_3SNa$ Found: 538.1398 m/z error [ppm]: −2.84 Calculated: 538.1383 m/z.

Triphenyphosphine gold *N*,*N*-dibenzy-*N*[(trifluoromethyl)-sulfonyl]-(*D*)-tryptophanamide (4). Silver carbonate (0.110 g, 0.40 mmol) was added to a solution of *N*,*N*-dibenzyl-*N*-[(trifluoromethyl)sulfonyl]-(*D*)-tryptophanamide **4** (0.114 g, 0.22 mmol) in dichloromethane (2.52 mL) at 0 °C and stirred for 5 min. Triphenylphosphine gold chloride (0.110 g, 0.22 mmol) was added and the reaction mixture stirred for a further 2 days at 10 °C. The reaction mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as an olive coloured solid (0.238 g, quant.). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61–6.67 (36H m, Ar), 4.26 (1H s, 2-H), 4.16 (2H d, J = 14.3, 12, 13-H), 3.80 (2H, d, J = 14.3, 12, 13-H), 3.57 (2 H, dd, J = 9.8, 14.0, 3-H), 3.12 (2 H, dd, J = 4.5, 14.1, 3-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.9 (s, 1-C), 140.1 (s, Ar), 135.7 (s, 11-C), 134.07 (d, J = 13.7, Ar), 131.9 (s, Ar), 129.1 (d, J = 12.1, Ar), 128.9 (s, Ar), 128.1 (s, Ar), 128.0 (s, Ar), 127.5 (s, Ar), 127.3 (s, Ar), 126.8 (s, 6-C), 123.2 (s, 5-CH), 121.7 (s, 9-CH), 119.3 (s, 8-CH), 118.9 (s, 7-CH), 112.2 (s, 10-CH), 110.7 (s, 4-CH), 67.2 (s, 2-CH), 54.7 (s, 12, 13-CH_2), 26.8 (s, 3-CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 33.00 (s, 1), 29.92 (s, 11). IR (diamond, ν_{MAX}, cm^{-1}) 2920 (NH st), 2019.56 (Ar comb), 1685 (C═O st amide), 1437 (H–C–H st as) 1181 (S–O st as), 1101 (S–O st sy). $[\alpha]_D^{21}$ = 57.7 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{44}H_{39}AuF_3N_3O_3PSNa$ Found: 974.2110 m/z error [ppm]: −4.95 Calculated: 974.2062 m/z.

***N*^{2}-[(Benzyloxy)carbonyl}-*N*^{1}-[(trifluoromethyl)sulfonyl]-(L)-leucinamide.** *N*-Benzoxycarbonyl-(L)-leucine (0.100 g, 0.377 mmol), triflic amine (56.2 mg, 0.377 mmol) and HOBt·H_2O (57.7 mg, 0.377 mmol) were dissolved in dichloromethane and cooled to 0 °C. EDC (60.0 mg, 0.386 mmol) was added and the mixture stirred for 15 min at 0 °C and then at room temperature for a further 3 days. The precipitate was

filtered off and the filtrate concentrated under reduced pressure. The residue was dissolved in ethyl acetate (5 mL) and washed with 1 M citric acid (3 mL), a saturated solution of sodium carbonate (3 mL), brine (3 mL) and dried over anhydrous magnesium sulphate and filtered. The organic layer was concentrated under reduced pressure. Purification by column chromatography (diethyl ether) afforded the title compound as a white solid (79.4 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33–7.16 (5H, m, Ar), 5.56 (1H, s, NH), 5.25–4.80 (2H m, 3-H), 4.06 (1H, s, 1-H), 3.69 (1H, br s, NH), 1.63–1.32 (3H m, 3, 4-H), 0.81 (6H, s, 5, 6-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 181.7 (2-C), 157.3 (9-C), 135.8 (11-C(Ar)), 128.4 (12, 14, 16-CH(Ar)), 128.1 (8-CF_3), 127.8 (13, 15-CH(Ar)), 67.3 (10-CH_2), 56.8 (1-CH), 40.8 (3-CH_2), 24.6 (4-CH), 22.7 (6-CH_3), 21.6 (5-CH_3). M.p.: 51–53 °C. IR (diamond, ν_{MAX}, cm^{-1}) 3393 (NH st), 2020 (Ar comb), 1704, 1622 (C═O st amide), 1292 (CO–O st), 1181 (S–O st as), 1124 (S–O st sy). $[\alpha]_D^{22}$ = 41.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{15}H_{19}F_3N_2O_5SNa$ Found: 419.0860 m/z error [ppm]: −0.26 Calculated: 419.0859 m/z.

Triphenylphosphine gold N^2-[(benzyloxy)carbonyl}-N^1-[(trifluoromethyl)sulfonyl]-(L)-leucinamide (3). Silver carbonate (0.126 g, 0.46 mmol) was added to a solution of (*S*)-benzyl(4-methyl-1-oxo-1-trifluoromethylsulfonamido)pentan-2-yl)carbamate (0.100 g, 0.25 mmol) in dichloromethane (C = 0.1 M, 2.52 mL) at 0 °C and stirred for 5 min. Triphenylphosphine-gold chloride (0.125 g, 0.25 mmol) was added and the resultant mixture stirred for 2 days at 0 °C. The reaction mixture was filtered through Celite and the solvent evaporated under reduced pressure to give the corresponding compound as a pink solid (0.213 g, quantitative). ^{1}H NMR (500 MHz, $CDCl_3$) δ = δ = 7.64–7.28 (20H, m, Ar), 5.16–4.97 (3H m, 10, 1-H), 1.87–1.66 (2H m, 3, 4-H), 1.61–1.52 (1H m, 3-H), 0.86 (3H, d, J = 6.5, 5-H), 0.73 (3H, d, J = 5.9, 6-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 178.2 (2-C), 155.9 (9-C), 136.39 (s, Ar), 134.3 (s, Ar), 134.2 (s, Ar), 134.1 (s, Ar), 132.3 (s, Ar), 132.3 (s, Ar), 132.1 (s, Ar), 132.0 (s, Ar), 131.9 (s, Ar), 131.9 (s, Ar), 131.57 (s, Ar), 129.5 (s, Ar), 129.4 (s, Ar), 129.2 (s, Ar), 129.1 (s, Ar), 129.0 (s, Ar), 128.8 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 127.99 (s, Ar), 127.83 (s, Ar), 127.48 (s, Ar), 127.35 (s, Ar), 124.29 (s, 8-CF), 121.71 (s, 8-CF), 119.13 (s, 8-CF), 116.54 (s, 8-CF), 66.8 (10-CH_2), 55.8 (1-CH), 43.0 (3-CH_2), 24.7 (4-CH), 23.2 (6-CH_3), 21.6 (5-CH_3). ^{31}P NMR (161 MHz, $CDCl_3$) δ = 31.1 (26%), 30.6 (74%). IR (diamond, ν_{MAX}, cm^{-1}) 3316 (NH st), 1982 (Ar comb), 1702 (C═O st amide), 1310 (CO–O st), 1180 (S–O st as), 1121 (S–O st sy). $[\alpha]_D^{25}$ = 29.3 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{33}H_{33}AuF_3N_2O_5PS$ Found: 877.1453 m/z error [ppm]: −10.85 Calculated: 877.1385 m/z.

(*S*)-2-((Diphenylphosphino)methyl)pyrrolidine-1-sulfonic acid. (*S*)-Hexahydropyrrolo[1,2-*b*]isothiazole 1,1-dioxide[32] (0.850 g, 5.21 mmol) was added to a solution of diphenylphosphine-lithium (5.21 mmol, C = 0.42 M) in dry tetrahydrofuran (12.4 mL). The reaction mixture was stirred for 3 h and quenched with 8 mL of water. The crude residue was extracted with dichloromethane (3 × 10 mL). The organic layers were combined and concentrated under reduced pressure. Purification by column chromatography ([10 : 90], methanol–dichloromethane) afforded the title compound as a colourless solid (1.648 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94–6.95 (10H, m, Ar), 3.76 (1H, s, 2-H), 3.32–2.80 (3H, m, 1, 5-H), 2.03 (1H, s, 1-H), 1.77 (1H, s, 3-H), 1.52 (3H, s, 3, 4-H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 139.1 (s, Ar), 139.0 (s, Ar), 132.8 (s, Ar), 132.6 (s, Ar), 128.5 (s, Ar), 128.4 (s, Ar), 128.4 (s, Ar), 128.3 (s, Ar), 128.3 (s, Ar), 58.8 (d, J = 21.0, 2-CH), 50.2 (s, 5-CH_2), 35.6 (s, 1-CH_2), 32.0 (s, 3-CH_2), 24.3 (s, 4-CH_2). ^{31}P NMR (243 MHz, $CDCl_3$) δ = −21.26 (s). M.p.: 120–121 °C. IR (diamond, ν_{MAX}, cm^{-1}) 1433 (H–C–H st as), 1174 (–SO_3^- st as), 1041 (–SO_3^- st sy). $[\alpha]_D^{22}$ = −50.4 (c = 1.0 in dichloromethane). Acc. Mass (FAB): $C_{17}H_{20}NaNO_3PS$ Found: 372.0803 m/z error [ppm]: −2.42 Calculated: 372.0794 m/z.

(L)-(−)-2-[(Diphenylphosphino)methyl]pyrrolidine (19). Deoxygenated 32% HCl (2 mL) was added to a round bottomed flask containing (*S*)-2-((diphenylphosphino)methyl)pyrrolidine-1-sulfonic acid (100 mg, 0.30 mmol) under nitrogen and stirred for 16 h at 85 °C. After cooling, the reaction was neutralized by a solution of potassium hydroxide to pH = 12 and extracted with dichloromethane (3 × 7 mL). The reaction mixture was concentrated under reduced pressure to give the title compound as a yellow oil (53 mg, 65%). All data are identical to those reported.[33]

General procedure

5,8a-Dimethyl-7,8,8a,9,10,10a-hexahydroanthracen-1-ol (14). (*E*)-2-(3-Methyloct-2-en-6-yn-1-yl)phenol (50 mg, 0.24 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.48 mL, 0.5 M) was added and the mixture stirred for around 2 minutes. The catalyst was added and the reaction mixture stirred for the appropriate time at room temperature. The solvent was concentrated under reduced pressure. Purification by column chromatography ([99 : 1], cyclohexane–ethyl acetate) afforded the title compound as a pale yellow oil.

Methyl 1-acetyl-2-methylenecyclopentanecarboxylate (12a). Methyl 2-acetylhept-6-ynoate (50 mg, 0.27 mmol) was placed in a dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 mL, 0.4 M) was added and the reaction mixture stirred for 2 minutes. The catalyst (16.5 mg, 0.014 mmol, 0.05 mol%) was added and the reaction mixture stirred for the appropriate time at the corresponding temperature. The solvent was concentrated under reduced pressure. Purification by column chromatography ([99 : 1], cyclohexane–ethyl acetate) afforded the title compound as a clear yellow oil.

Ethyl 1-benzoyl-2-methylenecyclopentanecarboxylate (12b). Ethyl 2-benzoylhept-6-ynoate (71 mg, 0.27 mmol) was placed in a flame dried round bottom flask under nitrogen. The appropriate dry solvent (0.69 mL, 0.4 M) was added and the mixture stirred for 2 minutes. The catalyst was added and the reaction mixture stirred for the appropriate time at the corresponding temperature. The solvent was concentrated under reduced pressure. Purification by column chromatography ([95 : 5], PET–ethyl acetate or diethyl ether) afforded the title compound as a colourless oil (65 mg, 91%).

DOSY experiments

Diffusion ordered spectra were acquired on a Varian VNMRS 600 equipped with an AutoX DB probe using the one-shot sequence of Pelta *et al.* (M. D. Pelta, G. A. Morris, M. J. Stchedroff and S. J. Hammond, A one-shot sequence for high resolution diffusion-ordered spectroscopy, *Magn. Reson. Chem.*, 2002, **40**, S147–S152) with 15 gradient increments equally spaced in g^2 between 0.0226 T m^{-1} and 05424 T m^{-1}. 32 Transients were recorded per gradient point. The data were subsequently processed using the DOSYToolbox package (M. Nilsson, The DOSY Toolbox: a new tool for processing PFG NMR diffusion data, *J. Magn. Reson.*, 2009, **200**, 296–302). Samples were placed in 3 mm diameter NMR tubes so as to limit the formation of convection currents and reduce phase errors during the pulse sequence and subsequent analysis.

Freezing point depression experiments

Gold complex **6a**/**6b** (88.0 mg) was dissolved in 1,2-dibromoethane (3.6890 g). The experimental temperature depression obtained (0.433 °C) was taken as the average of three experiments.

Gold complex **7** (58.5 mg) was dissolved in 1,2-dibromoethane (3.9060 g). The experimental temperature depression obtained (0.133 °C) was again taken as the average of three experiments.

Crystallography

All crystallographic details for compounds **6b**, **7**, **15** and **18** are provided in the ESI.†

Acknowledgements

Financial support from a Bader award is gratefully acknowledged. The authors also wish to thank Dr J. Turner, Dr N. Tsoureas, Prof. M. Bagley and Prof. P.J. Parsons for useful discussions, Prof. G. Cloke for providing access to a high precision temperature probe and Dr Alaa Abdul Sadaa for the Mass Spectrometry Service at the University of Sussex.

Notes and references

1 Z. Gao, Y. Li, J. P. Cooksey, T. N. Snaddon, S. Schunk, E. M. E. Viseux, S. M. McAteer and P. J. Kocienski, *Angew. Chem., Int. Ed.*, 2009, **48**, 5022–5025.
2 A. Hashmi, *Gold Bull.*, 2004, **37**, 51–65.
3 N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133–4136.
4 J. H. Teles, S. Brode and M. Chabanas, *Angew. Chem., Int. Ed.*, 1998, **37**, 1415–1418.
5 T. J. Brown and R. A. Widenhoefer, *Organometallics*, 2011, **30**, 6003–6009.
6 C.-M. Chao, E. Genin, P. Y. Toullec, J.-P. Genêt and V. Michelet, *J. Organomet. Chem.*, 2009, **694**, 538–545.
7 F. Mohr, *Gold chemistry: applications and future directions in the life sciences*, Wiley-VCH, 2009.
8 *Modern Supramolecular Gold Chemistry: Gold-Metal Interactions and Applications*, ed. A. Laguna, Wiley-VCH, 1st edn, 2008.
9 C. Khin, A. S. K. Hashmi and F. Rominger, *Eur. J. Inorg. Chem.*, 2010, 1063–1069.
10 J. Vicente, A. Arcas, P. G. Jones and J. Lautner, *J. Chem. Soc., Dalton Trans.*, 1990, 451–456.
11 J. Vicente, A. Arcas, M. Mora, X. Solans and M. Font-Altaba, *J. Organomet. Chem.*, 1986, **309**, 369–378.
12 R. Uson, A. Laguna, J. Vicente, J. Garcia, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1981, 655–657.
13 S. J. Berners-Price, P. S. Jarrett and P. J. Sadler, *Inorg. Chem.*, 1987, **26**, 3074–3077.
14 K. Saito, T. Tsukuda, K. Matsumoto and T. Tsubomura, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 533–535.
15 C. D. Delfs, H. J. Kitto, R. Stranger, G. F. Swiegers, S. B. Wild, A. C. Willis and G. J. Wilson, *Inorg. Chem.*, 2003, **42**, 4469–4478.
16 A. Bayler, A. Schier and H. Schmidbaur, *Inorg. Chem.*, 1998, **37**, 4353–4359.
17 P. C. Healy, B. T. Loughrey, M. L. Williams and P. G. Parsons, *J. Inorg. Biochem.*, 2010, **104**, 625–631.
18 M. C. Brandys and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2001, **123**, 4839–4840.
19 H. Schmidbaur, R. Herr, G. Mueller and J. Riede, *Organometallics*, 1985, **4**, 1208–1213.
20 J. M. Forward, Z. Assefa, R. J. Staples and J. P. Fackler, *Inorg. Chem.*, 1996, **35**, 16–22.
21 H. Schmidbaur, T. Pollok, G. Reber and G. Müller, *Chem. Ber.*, 1988, **121**, 1345–1348.
22 D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard and F. D. Toste, *Nat. Chem.*, 2009, **1**, 482–486.
23 B. N. Nguyen, L. A. Adrio, E. M. Barreiro, J. B. Brazier, P. Haycock, K. K. M. Hii, M. Nachtegaal, M. A. Newton and J. Szlachetko, *Organometallics*, 2012, **31**, 2395–2402.
24 E. L. Noey, Y. Luo, L. Zhang and K. N. Houk, *J. Am. Chem. Soc.*, 2012, **134**, 1078–1084.
25 J. Kennedy-Smith, S. Staben and F. Toste, *J. Am. Chem. Soc.*, 2004, **126**, 4526–4527.
26 P. Y. Toullec, T. Blarre and V. Michelet, *Org. Lett.*, 2009, **11**, 2888–2891.
27 C. S. Johnson Jr., *Prog. Nucl. Magn. Reson. Spectrosc.*, 1999, **34**, 203–256.
28 M. Nilsson, *J. Magn. Reson.*, 2009, **200**, 296–302.
29 R. Huo, R. Wehrens, J. V. Duynhoven and L. M. C. Buydens, *Anal. Chim. Acta*, 2003, **490**, 231–251.
30 A. Macchioni, G. Ciancaleoni, C. Zuccaccia and D. Zuccaccia, *Chem. Soc. Rev.*, 2008, **37**, 479–489.
31 J. Frelek, A. Fryszkowska, M. Kwit and R. Ostaszewski, *Tetrahedron: Asymmetr.*, 2006, **17**, 2469–2478.
32 D. Alker, K. J. Doyle, L. M. Harwood and A. McGregior, *Tetrahedron: Asymmetr.*, 1990, **1**, 877–880.
33 M. Kanai, Y. Nakagawa and K. Tomioka, *Tetrahedron*, 1999, **55**, 3843–3854.